

$\Delta S$ : change in entropy.

$\Delta G$ : change in Gibbs free energy.

Note:  $\Delta S$  is a part of  $\Delta G$ .

So,

as randomness  $\uparrow \Rightarrow \Delta S \uparrow$

### State of matters

Solid: low  $S$  due to hardness of attraction forces.

Liquid:

Gas: High  $S$  due to weakness of attraction forces.

### Spontaneous Reaction:

- A reaction that happens without any external conditions like: Ice to water.

### non-Spontaneous Reaction:

- A Reaction that happens with (by) the effect of external conditions.

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Section 45

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## → second law of thermodynamics

- every spontaneous change is accompanied by increase in  $S$

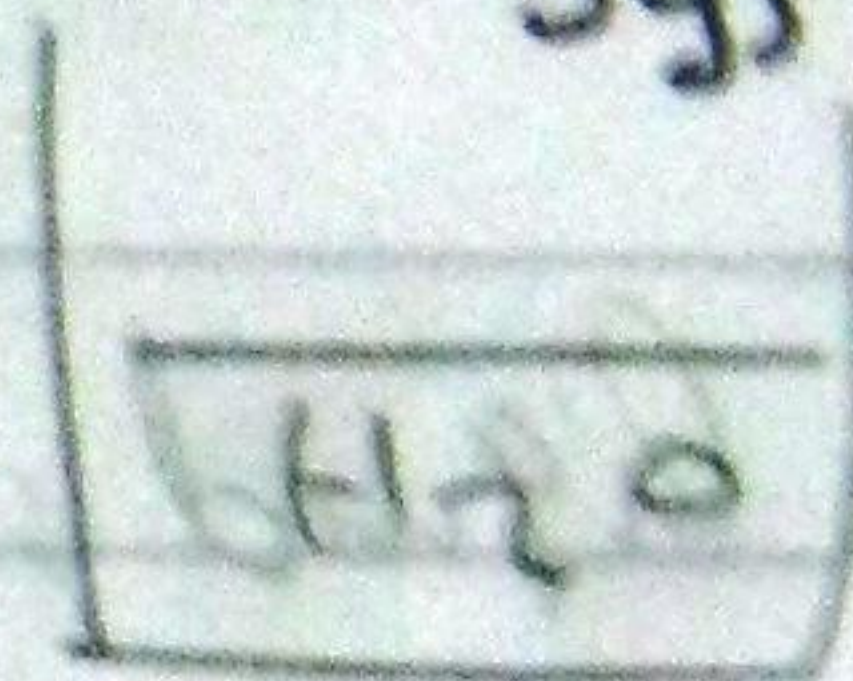
Solid  $\rightarrow$  liquids  
low  $S$       high  $S$   
 $\Delta S = +ve$   
"spontaneous"

liquid  $\rightarrow$  solid  
high  $S$       low  $S$   
 $\Delta S = -ve$   
"non-spontaneous"

- system: The matter which I study  $\rightarrow \Delta S_{sys}$ .

AT figure

H<sub>2</sub>O is the system.



- surroundings: the objects that surround the system

$\rightarrow \Delta S_{surr}$

AT figure

All conditions and the container.

$$\Delta S_{Total} = \Delta S_{system} + \Delta S_{surrounding}$$

liquid  $\rightarrow$  solid  
 $\Delta S_{sys} = -ve$

$\Delta S_{surr} = +ve$

→ As  $\Delta S_T \uparrow = +ve \Rightarrow$  spon.

$\Rightarrow \Delta G = -ve, \neq 0$

→ As  $\Delta S_T = -ve \Rightarrow$  non-spon.

$\Rightarrow \Delta G = 0$

→ As  $\Delta S_T \downarrow = 0 \Rightarrow$  equilibrium

$\Rightarrow \Delta G = +ve, \neq 0$



ex Water  $\rightarrow$  ice  $\frac{H\Delta}{T}$  at ;  $+1^\circ\text{C}$ , zero,  $-1^\circ\text{C}$

$(+1^\circ\text{C})$  :  $\Delta S_{\text{sys.}} = -\text{ve}$  ,  $\Delta S_{\text{surr.}} = +\text{ve}$

$\therefore \Delta S_T = -\text{ve}$

$\therefore$  Reaction is non-spontaneous.

$(-1^\circ\text{C})$  :  $\Delta S_{\text{sys.}} = -\text{ve}$  ,  $\Delta S_{\text{surr.}} = +\text{ve}$

$\therefore \Delta S_T = +\text{ve}$

$\therefore$  Reaction is spontaneous.

$(0^\circ\text{C})$  :  $\Delta S_{\text{sys.}} = -\text{ve}$  ,  $\Delta S_{\text{surr.}} = +\text{ve}$

$\therefore \Delta S_T = \text{zero}$

Note :  $\rightarrow \Delta S_{\text{sys.}} = -\text{ve}$  ,  $\Delta S_{\text{surr.}} = +\text{ve}$  at all conditions as it depends on randomness.

$\rightarrow$  The energy that the system release the surrounding absorb it.

$\rightarrow T$  : is +ve at all conditions.

$\Delta G$

- change in Gibbs free energy
- used to know that reaction is (spontaneous or non spontan.).

$\Delta G = -T \Delta S_T$



$$\boxed{\Delta S_{\text{surr}} = - \frac{\Delta H}{T}} \quad \text{--- (1)}$$

$$\Delta S_T = \Delta S_{\text{sys}} + \Delta S_{\text{surr.}} \quad \text{--- (2)}$$

By (1), (2)

$$\Delta S_T = \Delta S_{\text{sys}} - \frac{\Delta H}{T} \times (-T)$$

$$-T \Delta S_T = -T \Delta S_{\text{sys}} + \Delta H$$

$$\therefore \boxed{\Delta G = -T \Delta S_T}$$

$$\therefore \boxed{\Delta G = \Delta H - T \Delta S_{\text{sys}}} \Rightarrow \text{Imp.}$$

Note : we can know that Reaction is (spont. or non. spont.) by  $\Delta S$  or  $\Delta G$ . but  $\Delta G$  is more practical than  $\Delta S$  at it is hard to calculate ( $\Delta S_{\text{sys.}}$ ,  $\Delta S_{\text{surr.}}$ ).



$$\Delta S_{\text{sys.}} = \Delta S_p - \Delta S_r$$

Note : Any Boiling point or Freezing point represent the condition of equilibrium.

(Boiling of water)  $\rightarrow 100^\circ\text{C}$

(Freezing of water)  $\rightarrow 0^\circ\text{C}$

$$\boxed{\Delta H_{\text{reaction}} = \Delta H_{f(P)} - \Delta H_{f(R)}}$$

$\Delta G_f(\text{element}), \Delta H_f(\text{any element}) = 0 \Rightarrow \text{Imp.}$

$$\boxed{\Delta G_{\text{reaction}} = \Delta G_{f(P)} - \Delta G_{f(R)}}$$



measured	$\Delta H$	measured	$\Delta H^\circ$
at	$\Delta E$	at	$\Delta E^\circ$
any	$\Delta S$	standard	$\Delta S^\circ$
conditions	$\Delta G$	conditions	$\Delta G^\circ$

$P = 1 \text{ atm}$   
 $T = 25^\circ \text{C}$

$$\rightarrow \Delta G = \Delta H - T\Delta S \quad \rightarrow \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$\rightarrow$  Note To calculate any term of the law  
 $(T = 298^\circ \text{K})$

- To calculate the normal Boiling point  
 $(\Delta G = 0)$ .

$\Delta H$ :  $\Delta H = \Delta E + \Delta nRT \Rightarrow \text{Solid or liquid or gas.}$   
 $\Delta H = \Delta H_f(P) - \Delta H_f(R) \Rightarrow \text{Compound or element}$   
 $\Delta H = \Delta G + T\Delta S$

$\Delta E$ :  $\Delta H = \Delta E + \Delta nRT$   
 $\Delta E = q_v \Rightarrow \text{Per one mole.}$   
 $\Delta n = n_p - n_r \Rightarrow \text{Gas.}$   
 $\Delta E = q - w.$

$\Delta S$ :  $\Delta S = \Delta S_p - \Delta S_r \Rightarrow (\text{Element} \neq 0)$

$\Delta G$ :  $\Delta G = \Delta G_f(P) - \Delta G_f(R)$   
 $\Delta G = \Delta H - T\Delta S.$

Note Heat of Reaction:  $\Delta H_{\text{reaction}}$ .